

Exhibit 2

Journal of Molecular Catalysis, 34 (1986) 345 - 354

345

**LINEAR DIMERIZATION OF PROPYLENE AND 1-BUTENE
CATALYZED BY (η^3 -4-CYCLOOCTENE-1-YL)-
(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO)NICKEL****DAVID L. BEACH,* JOHN E. BOZIK, CHING-YONG WU and YURY V. KISSIN***Gulf Research and Development Company, P.O. Drawer 2038, Pittsburgh, PA 15230
(U.S.A.)*

(Received April 13, 1985; accepted September 25, 1985)

Summary

The dimerization and oligomerization of propylene and 1-butene in the presence of homogeneous Group VIII transition metal catalysts has been extensively studied. In most cases the products obtained are mixtures of isomers in which branched species predominate, in accordance with preferred anti-Markownikov addition pathways.

In what is perhaps the most well-defined catalyst system to date, a family of substituted fluoroacetylacetonate cyclooctenyl nickel complexes, 1-butene is oligomerized to up to 82% linear octenes. Propylene and 1-butene are dimerized to predominantly normal alkenes using homogeneous hydrocarbon solutions of (η^3 -4-cyclooctene-1-yl)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)nickel. Two disadvantages of this catalyst system are its relatively low activity and rapid deactivation on storage.

In this paper, an improved synthesis of the catalyst is reported, in addition to a method of catalyst storage which virtually eliminates deactivation. A comprehensive olefin dimerization reaction scheme is formulated on the basis of detailed gas chromatographic analyses of propylene and 1-butene dimers. The relative amounts of the materials identified allow conclusions to be drawn on relative rates for the competing olefin insertion, β -elimination pathways.

Introduction

The dimerization and oligomerization of propylene and 1-butene in the presence of homogeneous Group VIII transition metal catalysts has been extensively studied [1-4]. In most cases, the products obtained are mixtures of isomers in which branched species predominate, in accordance with preferred anti-Markownikov addition pathways.

In what is perhaps the most well-defined catalyst system to date, a family of substituted fluoroacetylacetonate cyclooctenyl nickel compounds,

0304-5102/86/\$3.50

© Elsevier Sequoia/Printed in The Netherlands

346

1-butene is oligomerized to up to 82% linear octenes [5]. Two disadvantages of this catalyst are its relatively low activity and rapid deactivation on storage.

In this paper, we discuss mechanistic aspects of oligomerization (primarily dimerization) of propylene and 1-butene using this catalyst. Detailed identification of the reaction products by GC allowed elucidation of primary and secondary processes, including comparisons of relative rates for competing pathways. Additionally, a catalyst storage method which virtually eliminates catalyst deactivation is mentioned.

Experimental

All manipulations of air- and water-sensitive materials were performed in a Vacuum Atmospheres glove box containing either purified nitrogen or argon atmosphere. Oxygen and moisture levels were monitored continuously and always maintained at <10 ppm; typical levels were <3 ppm for oxygen and <1 ppm for water. Those experiments which involved manipulations sufficiently difficult to preclude the use of a glove box were performed using a Schlenk line and argon purified by passage through a column containing molecular sieves, hydrogen-reduced BASF R8-11 copper catalyst at 100 °C as an oxygen scavenger, and an additional column of molecular sieves. All solvents were purified by distillation from appropriate drying agents under inert atmosphere. Chemical reagents used were of the highest purity available from conventional chemical supply companies.

(η^3 -4-Cyclooctene-1-yl)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)nickel
($Ni(\pi-C_8H_{17})(acac-f_6)$).

This material was prepared from bis(1,5-cyclooctadiene)nickel and hexafluoroacetylacetone using a modification of the method described by Bogdanovic *et al.* [7].

Inside a glove box, 6.71 g (24.4 mmol) of bis(1,5-cyclooctadiene)nickel and 6.69 g (32.2 mmol) of hexafluoroacetone were dissolved in 50 ml toluene and stirred in a 250 ml round-bottom flask at 25 °C for 2 h and at 40 °C for 2 h. The toluene was removed via rotary evaporation and the residue stirred with 50 ml pentane for 30 min. The insoluble material was filtered off and the pentane filtrate evaporated to dryness to yield 8.86 g (54% yield) of product. Recrystallization from toluene/pentane at low temperature afforded the desired material with physical and spectroscopic properties identical to literature values [5].

Dimerization of propylene

Dimerization experiments were performed in a 300 ml stainless steel autoclave equipped with Magnedrive stirrer and internal cooling coils (Autoclave Engineers, Erie, PA). The autoclave was carefully flushed with dry, oxygen-free argon prior to each experiment by successive evacuation, argon back-fill cycles.

A typical experiment was performed by charging 1.0 mmol $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$ in 50 ml toluene to the evacuated autoclave via syringe. Propylene was charged to a pressure of 100 psig and maintained at that pressure throughout the course of the reaction. The autoclave was rapidly heated to 70 °C and maintained at this temperature for 8 h via an automatic temperature control unit which supplied heating or cooling on demand. After the reaction, unreacted propylene was vented and the liquid product analyzed for C_6 dimers, C_9 trimers and C_{12} tetramers by GLC on a 22.5 ft \times 1/8 in stainless steel column packed with 25% SE-31 on Chromosorb W.

Dimerization of 1-butene

1.0 Mmol $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$ in 50 ml solvent was charged via syringe into the purged, evacuated autoclave. 1-Butene was charged to the stirring autoclave at 25 °C and at cylinder pressure for 35 min. The 1-butene cylinder valve was closed and the autoclave was heated rapidly to 70 °C to start the dimerization. The pressure inside the autoclave usually rose from less than 25 psi to ~ 75 psi before starting to fall again as the dimerization took place. After 8 h at 70 °C, the autoclave was cooled to 25 °C and the gas inside the autoclave was vented. The product was removed and analyzed by GLC on a 22.5 ft \times 1/8 in stainless steel column packed with 25% SE-31 on Chromosorb W.

Hydrogenation of butene dimers

The product from the dimerization of 1-butene was washed once with half its volume of 20% aqueous HCl to destroy the catalyst, washed once with half its volume of distilled water to remove HCl residue, and dried for 30 min with anhydrous MgSO_4 . The product was filtered to remove MgSO_4 and evaporated on a Rotovac to remove unreacted 1-butene and some of the solvent used. It was then hydrogenated at 25 °C and 40 psig H_2 pressure using 0.1% PtO_2 as catalyst until the uptake of H_2 had stopped. The hydrogenated product was again analyzed by GLC using the same SE-31 column. Authentic samples were used for identification and calibration.

Gas chromatographic analysis

A Hewlett-Packard HP5880A gas chromatograph equipped with a flame ionization detector was used to obtain chromatographic data. The columns were 50 m \times 0.02 mm i.d. fused silica capillary coated with 0.50 micron film of crosslinked methyl silicone and squalene. Helium carrier gas was used at a flow of 1 ml min^{-1} . The column oven temperature was programmed from 40 °C to 280 °C at 5 °C min^{-1} ; detector and injector temperatures were held at 350 °C. The samples were dissolved in CS_2 in a 1:5 ratio before injecting into the chromatograph.

Results

1-Butene dimerization

Figure 1 shows a gas chromatogram of 1-butene dimers with $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$ as a catalyst. Peak assignment in the chromatogram is

348

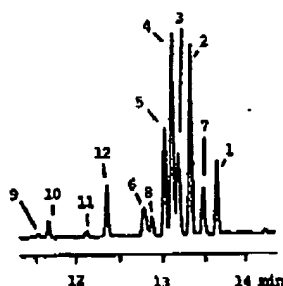


Fig. 1. Gas chromatogram of 1-butene dimers with $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$ catalyst.

TABLE 1

Peak assignment in gas chromatogram of 1-butene dimers obtained at 70 °C

Peak No.	Assignment	Content in total dimer mixture (wt.%)
1	<i>cis</i> -2-octene	8.6
2	<i>trans</i> -2-octene	21.1
3	<i>cis</i> -3- + <i>cis</i> -4-octenes	12.6
4	<i>trans</i> -3-octene	22.0
5	<i>trans</i> -4-octene	11.8
6	2-ethyl-1-hexene	5.1
7, 8	<i>cis</i> - + <i>trans</i> -3-methyl-2-heptenes	8.3
	<i>cis</i> - + <i>trans</i> -3-methyl-3-heptenes	
9 - 12	branched olefins	10.5

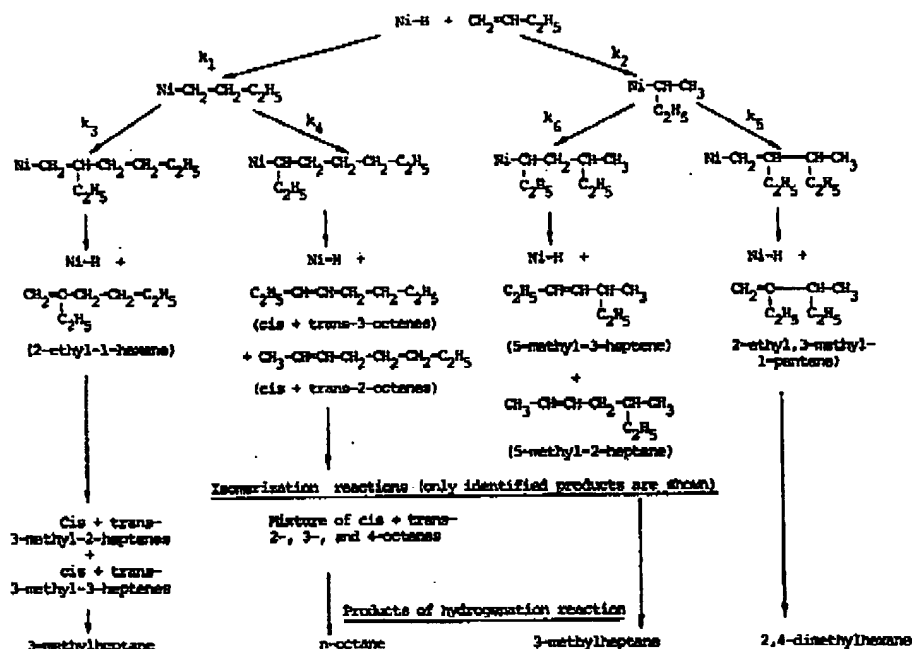
presented in Table 1. The reaction scheme of 1-butene dimerization emerging from these data is shown in Scheme 1.

In the scheme, nickel hydride species are assumed as catalytic centers. There are two types of 1-butene insertion, primary (reactions with rate constants k_1 , k_3 and k_5) and secondary (k_2 , k_4 and k_6). The reaction scheme is complicated by the fact that examined nickel-containing compounds are potent catalysts for olefin double bond isomerization. Two types of such isomerization products were found in the dimers: *trans*-4-octene (obtained by isomerization of 2- and 3-octenes) and a series of products of double bond isomerization of 2-ethyl-1-hexene, viz, *cis*- and *trans*-3-methyl-2- and 3-heptenes.

Unfortunately, the GC retention times of the products of 2-ethyl-1-hexene isomerization are very close to those of the butene dimerization primary products, making quantitative identification by GC difficult. In order to aid the GC analysis, the isomerization reaction of 2-ethyl-1-hexene was studied independently (isomerization over zeolite 13X at 55 °C).^{*} Two products of this reaction were identified as peak Nos. 7 and 8 in the chromatogram in Fig. 1 (see Table 1), and two other peaks are overlapped by peaks of *trans*-3-octene and *cis*-3- and -4-octenes. Gas chromatographic analysis of the hydrogenation products of these dimers indicates the presence of two

^{*}See p. 349.

349



Scheme 1. 1-Butene dimerization reaction pathways.

major products, n-octane (65%) and 3-methylheptane (35%). 2,4-Dimethylhexane is present in the mixture in minor amounts (0.14%), indicating a very low value of the k_6 rate constant, probably because of steric reasons. This allows the assignment of several minor peaks in the chromatogram (peaks 9 - 12) to *cis*- and *trans*-6-methyl-2- and -3-heptenes. Judging by the product distribution data given in Table 1, the reaction route characterized by rate constants k_2 and k_5 accounts only for ca. 10% of the total dimer content. This means that the primary insertion of 1-butene (rate constant k_1) into the Ni-H bond is ca. 9 times faster than the secondary insertion into this bond (rate constant k_2).

Quantitative evaluation of the relative significance of (k_1 , k_3) and (k_1 , k_4) routes is complicated by the fact (mentioned above) that peaks of some isomers for the products of 2-ethyl-1-hexene isomerization are overlapped by the peaks of linear octenes. If one assumes* that the distribution of these isomerization products of 2-ethyl-1-hexene is similar in reactions catalyzed by nickel complexes and zeolite 13X, then the ratio of the amounts of isomerization products of 2-ethyl-1-hexene (representing the (k_1 , k_3) route) and the amount of all linear octenes (representing the (k_1 , k_4) route) is ca. 0.22

*Although the isomerization mechanism with zeolites is, of course, different than with Ni, the isomerization products in this case are identical, and their distribution is thermodynamically determined.

350

(see Table 1). Thus, the following reaction rate constant ratios in Scheme 1 can be proposed: $k_1:k_2 = 9$; $k_3:k_4 = 0.22$; and $k_5:k_6 = 0.006$.

The effect of reactivity inversion (1-butene primary insertion is 9 times more probable in the case of the Ni—H bond but is ca. 4.6 times more probable in the case of the Ni—C bond) is likely due to the overlap of electronic factors favoring the primary insertion and that of steric factors which are negligible for the Ni—H bond, but play an important role in the case of the Ni—C bond.

Although isomerization of 1- to 2-butene proceeds with this catalyst, activity of 2-butene in codimerization with 1-butene is low due to steric reasons. Attempts to identify these codimers in the chromatogram (see Fig. 1) showed that their yield, if any, is <10%. For this reason, effects of 2-butene on the rate of 1-butene dimerization are negligible.

The effect of various additives, such as free ligand, on catalyst activity was explored. The results are shown in Table 2. Only triethylaluminum (TEA) increased the catalyst turnover number (by 8%). The addition of free ligand, 1,5-cyclooctadiene or hexafluoroacetylacetone, results in a decrease in activity, by 68% and 14% respectively. The use of a soluble Lewis acid, $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, also reduced catalyst activity by 31%.

TABLE 2

Effect of various additives in dimerization of 1-butene^a

Promoter	No additive	COD ^b	acac-f ₆ ^c	TEA ^d	$\text{BF}_3 \cdot \text{Et}_2\text{O}$
ratio promoter/Ni	0	0.2	2.0	0.25	2.0
mole % dimers	85.5	93.9	93.7	85.8	85.3
total product, g	32.4	10.4	27.6	35.1	22.4
turnover number	579	186	496	627	400

^aReaction conditions: $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$, 1 mol; solvent, 50 ml toluene; reaction time, 3 h; reaction temperature, 70 °C; initial pressure, 80 psig.

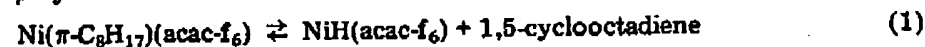
^b1,5-Cyclooctadiene.

^cHexafluoroacetylacetone.

^dTriethylaluminum.

The effect of reaction time is shown in Table 3. The dimerization of 1-butene is fastest during the first hour, after which catalyst decay becomes rapid.

Table 4 shows the effect of catalyst concentration on the dimerization of 1-butene. It is known that homogeneous nickel catalyst precursors containing hydrocarbon ligands possessing a β -hydrogen form active catalysts by β -hydride elimination to form nickel hydride species:



The data ([5], Table 2) support this mechanism. Addition of free 1,5-cyclooctadiene to the catalyst shifts the equilibrium in reaction (1) to the left,

TABLE 3

Effect of reaction time on dimerization of 1-butene^a

	1 h	2 h	3 h
mol% dimers	86.3	82.5	82.2
total product (g)	24.1	34.8	36.9
turnover number	430	621	659

^aReaction conditions: $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$, 1 mmol; solvent, 50 ml toluene; reaction time, 3 h; reaction temperature, 70 °C; initial pressure, 80 psi.

TABLE 4

Effect of catalyst concentration on dimerization of 1-butene^a

	0.5	1	2
catalyst ^b (mmol)			
total product (g)	32.0	43.0	62.6
dimers (mol%)	87.0	84.5	85.2
turnover number	1143	768	559
$[\text{dimers}]/(\text{cat mol})^{1/2}/(\text{mol})^{1/2}$	0.35	0.32	0.34

^aReaction conditions: solvent, 50 ml toluene; reaction temperature, 70 °C; reaction time, 3 h; initial pressure, 80 psig.

^b $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$

thus decreasing effective concentration of the active nickel hydride catalytic species. It follows that, with the equilibrium in reaction (1) shifted to the left, the catalyst activity should be approximately proportional to the square root of the catalyst concentration. This was confirmed experimentally, as shown in Table 4.

Catalyst stability

The catalyst, $\text{Ni}(\pi\text{-C}_8\text{H}_{17})(\text{acac-f}_6)$, is known to be unstable at room temperature and must be prepared shortly before use. Catalysts prepared *in situ* by reacting bis(1,5-cyclooctadiene)nickel with hexafluoroacetylacetone are not very active for the dimerization of 1-butene. The catalyst turnover frequency is only $15 \text{ mol (mol Ni)}^{-1} \text{ h}^{-1}$. The catalyst activity improves significantly to $330 \text{ mol (mol Ni)}^{-1} \text{ h}^{-1}$ when purified catalyst is used [5].

To facilitate routine experimentation, the rate of catalyst deactivation, as measured by 1-butene dimerization activity, was measured for several storage methods. Figure 2 shows data for the solid catalyst stored at room temperature under argon, as a toluene solution at room temperature, and as a toluene solution at 0 °C. As a solid at room temperature, the catalyst loses ca. 50% of its original activity after 10 days of storage. In toluene solution (17 wt.%) at room temperature, the catalyst showed an initial slower deactivation for 15 days, accelerating to lose 90% of its activity after 25 days.

The deactivation was accompanied by the formation of a heavy reddish-brown precipitate. Both catalyst deactivation and the formation of the pre-

352

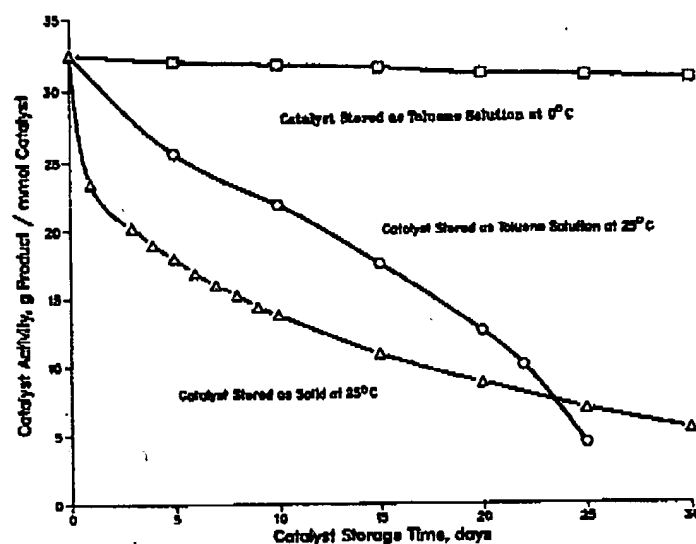
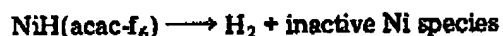


Fig. 2. Rate of catalyst deactivation for 1-butene dimerization.

precipitate can be explained by elimination of H_2 from the nickel hydride species formed in reaction (1):



When stored at 0 °C as a toluene solution, however, the catalyst retained 95% of its original activity after 30 days of storage.

Propylene dimerization with $Ni(\pi-C_8H_{17})(acac-f_6)$ catalyst

Table 5 shows the results of propylene dimerization at 70 °C using $Ni(\pi-C_8H_{17})(acac-f_6)$ as catalyst and cumene as solvent. The reaction time was varied from 30 min to 4 h to demonstrate that the catalyst was still active at the end of each experiment.

The average catalyst turnover rate was $700\ h^{-1}$ and turnover numbers were as high as 2700. The products were propylene dimers and trimers. Average linearity of propylene dimers was 87 mol%.

GC analysis of propylene oligomers allowed detailed evaluation of the reactions constituting propylene dimerization. Scheme 2 shows the principal reactions and allows elucidation of the reaction mechanism. The scheme is constructed analogously to Scheme 1 to allow detailed comparison of reaction steps in dimerization of propylene and 1-butene. Unfortunately, secondary double bond isomerization apparent from Scheme 2 makes difficult the precise determination of quantities of some primary dimerization products such as 1- and 2-hexenes, 2-methyl-1-pentene and 4-methyl-2-pentene. This makes the mechanistic data for propylene dimerization less dependable than those for 1-butene dimerization. Analysis of the GC data

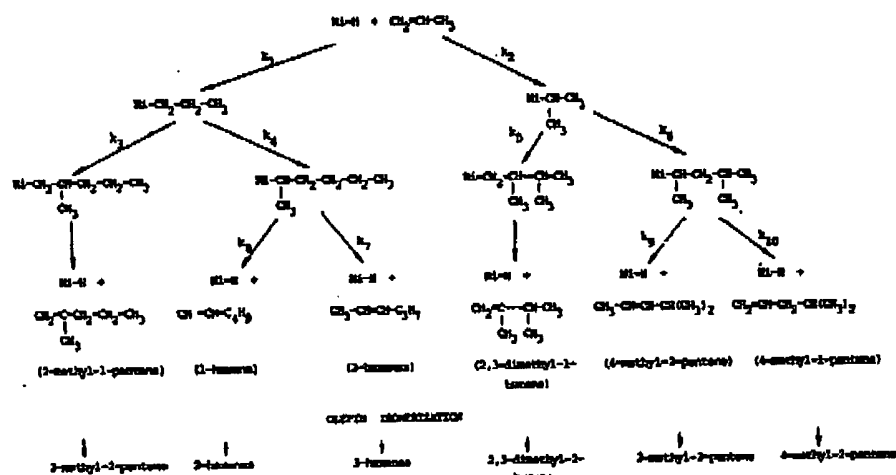
353

TABLE 5
Dimerization of propylene^a

	Run number			
	1	2	3	4
catalyst used (mmol)	1.0	1.0	0.5	0.5
propylene pressure (atm)	6.8	6.8	6.8	9.4
reaction time at constant pressure ^b (h)	0.5	2	2	4
total reaction time ^b (h)	3	3	3	4
total product (g)	80.2	68.3	41.8	57.0
mol% dimers	79.5	78.0	79.8	80.5
turnover number	719	1626	1990	2714

^aReaction conditions: solvent, 60 ml cumene; reaction temperature, 70 °C; reaction pressure, 100 - 138 psi; reaction time, 3 - 4 h; catalyst, Ni(π -C₆H₁₇)(acac-f₆).

^bPropylene pressure was maintained constant for the time indicated and then allowed to decrease.



Scheme 2. Propylene dimerization reaction pathways.

(presented in Table 6) gives the following rate constant ratios for the key steps:

- $k_1:k_2 = 14.2$ (the ratio of primary to secondary rate constants for propylene insertion into the Ni-H bond)
- $k_3:k_4 = 0.25$ (the ratio of primary to secondary rate constants for propylene insertion into the Ni-C bond in the Ni-CH₂-CH₂-CH₃ group)
- $k_5:k_6 = 0.18$ (the ratio of primary to secondary rate constants for propylene insertion into the Ni-C bond in the Ni-CH(CH₃)₂ group)

354

TABLE 6

Composition of propylene dimers

Olefin	Mol%
1-hexene	2.9
2-hexenes (<i>cis</i> + <i>trans</i>)	61.6
3-hexenes (<i>cis</i> + <i>trans</i>)	10.0
2-methyl-1-pentene	4.7
2-methyl-2-pentene	14.1
4-methyl-1-pentene	0.8
4-methyl-2-pentene (<i>cis</i> + <i>trans</i>)	4.7
2,3-dimethyl-1-butene	0.6
2,3-dimethyl-2-butene	0.4

$k_9:k_{10} = 7$ (the ratio of β -elimination rate constants from CH_2 and CH_3 groups)

Qualitatively, these ratios are close to those for 1-butene dimerization. However, lower steric requirements for the methyl group in the propylene molecule relative to the ethyl group in the 1-butene molecule result in decreased limitations for 'head-to-head' dimerization, as indicated by the difference in the $k_5:k_6$ ratios.

Products of propylene oligomerization always contain, in addition to dimers, a small amount of trimers. GC analysis of one of the samples showed that these trimers contained a relatively high concentration of linear products, ca. 40%. These linear trimers are *cis*- and *trans*-2-, -3-, and -4-nonenes. Such compounds cannot arise as primary propylene trimerization products. However, they can be explained as secondary reaction products formed from codimerization of propylene and 1-hexene produced in the reaction sequence (k_1 , k_4 , k_8) in Scheme 2. Another product of the codimerization, 2-methyl-1-octene, formed in a reaction sequence similar to (k_1 , k_3) in Schemes 1 and 2, was also identified and constituted ca. 1.5% of the trimers.

Hydrogenation of the trimers produced n-nonane (ca. 38%), methyl-octanes (ca. 55%), and dimethylheptanes (ca. 7%). These results confirm a significant contribution of the codimerization products to the total trimers.

References

- 1 W. Keim, A. Behr and M. Roper, in G. Wilkinson (ed.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon Press, Oxford, 1982, p. 371.
- 2 G. Henrici-Olive and S. Olive, *Coordination and Catalysis*, Verlag Chemie, New York, 1977, p. 186.
- 3 P. W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Vol 2, Academic Press, New York, 1975, p. 1.
- 4 R. F. Heck, *Organotransition Metal Chemistry*, Academic Press, New York, 1974, p. 84.
- 5 W. Keim, B. Hoffmann, R. Lodewick, M. Penckert, G. Schmitt, J. Fleischhauer and U. Meier, *J. Mol. Catal.*, 6 (1979) 79.
- 6 G. Henrici-Olive and S. Olive, *Angew. Chem. Int. Ed. Engl.*, 14 (1975) 104.
- 7 B. Bogdanovic, M. Kroner and G. Wilke, *Justus Liebigs Ann. Chem.*, 699 (1966) 1.